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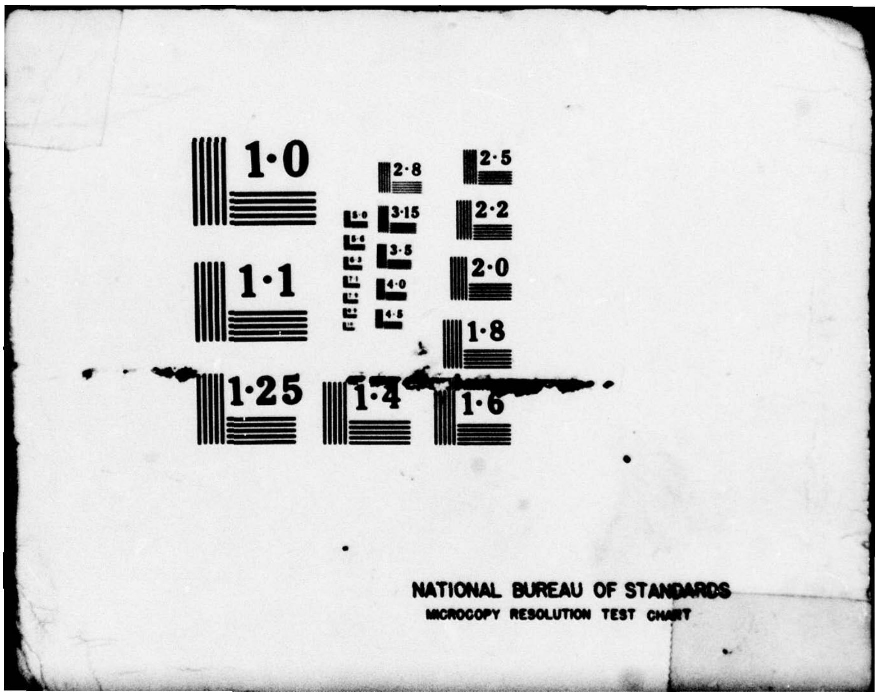
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AFML-TR-79-4034 LEVEL II

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PROCESSING FUNDAMENTALS FOR INTERCALATION OF GRAPHITE FIBERS

UNIVERSITY OF PENNSYLVANIA
OFFICE OF RESEARCH ADMINISTRATION
3451 WALNUT STREET
PHILADELPHIA, PENNSYLVANIA 19104

MAY 1979

TECHNICAL REPORT AFML-TR-79-4034
Final Report for Period 15 September 1977 through 15 September 1978

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AIR FORCE MATERIALS LABORATORY
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This technical report has been reviewed and is approved for publication.

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Project Monitor

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FOR THE COMMANDER

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Chemical kinetics of intercalation of carbon/graphite fibers with HNO_3/AsF_5 was determined. Fiber electrical conductivity increased by about an order of magnitude. Humidity testing of the bare fiber caused deintercalation as expected but the intercalated fibers were successfully incorporated into epoxy matrix

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composites which maintained their properties with time at room temperature.
microns
The expected increase of IR reflectivity at 10.6 μ for the intercalated fiber composite was not obtained. The remarkable observation was made that the electrical conductivity of composites was increased by a factor of about one hundred when filled to 55% with intercalated fibers having a seven fold increase in conductivity.

PREFACE

This report was prepared by the College of Engineering and Applied Science, University of Pennsylvania, Philadelphia, Pennsylvania 19104 under USAF Contract F33615-77-C-5182. It represents a collaborative effort between the Department of Electrical Engineering and Science and the Department of Chemical and Biochemical Engineering. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Mr. Roger E. Rondeau (AFML/LPJ) as Technical Monitor.

Work covered in this report was carried out from 15 September 1977 to 15 September 1978. The report was submitted by the University of Pennsyvlania in January 1979 for publication as an AFML Technical Report.

The Principal Investigators for this project were Professor F. Lincoln Vogel and Professor William C. Forsman. Most of the intercalation experiments were performed by Dr. Hossien Saatchi, a post-doctoral fellow. Electrical measurements were made by Dr. Claude Zeller, compositing was done by Messers Glenn Davis and Thomas Carroll. Important contributions to the chemical intercalation experiments were made by Dr. Helen Mertwoy. The difficult optical reflectivity measurements were done by Mr. Robert Winn of the Non-Metallic Materials Division of the Air Force Materials Laboratory. The highly oriented pyrolytic graphite used in the exploratory intercalation experiments was kindly donated

by Dr. Arthur Moore of Union Carbide Corp. Typing of the manuscripts was done by Mrs. Teresa Regan and Mrs. Rochelle Johnson.

This technical report has been reviewed and is approved for publication.

TABLE OF CONTENTS

SECTION I
INTRODUCTION

The Air Force has expressed a need for graphite-based fibers which exhibit higher electrical conductivity and infrared reflectance than fibers of pure graphite. Such fibers would be fabricated into composites. In order to be practical engineering materials, these composites must be stable in a normal atmosphere of nitrogen, oxygen, and water. Previous research indicates that fibers prepared by forming graphite intercalation compounds from graphite fibers are highly conducting and retain good mechanical properties.(1)

Graphite intercalation compounds are formed when molecules, atoms, or ions are inserted between the hexagonal plane of carbon atoms in the graphite lattice. The number of contiguous carbon layers separating two successive completely filled intercalant layers is called the "stage" of the intercalation compound. Evidence indicates that well defined stage compounds exist, but it is not uncommon for reactions to lead to "mixed-stage" compounds.

Although graphite intercalation compounds have been known for over 100 years, and have been studied intensively for 20 years, only recently has there been much serious research on the chemistry of the intercalation and deintercalation processes. The chemical methods used to intercalate graphite with strong acids (1,2) is well covered in the literature and so will not be repeated here. Previous work sponsored by the Air Force established that high reflectivity (3) in the infrared region of the spectrum, particularly at 10.6μ is obtained by intercalating graphite with AsF_5. Also, it has been shown that graphite-AsF_5 has high electrical conductivity (4).

The above mentioned work on AsF_5 intercalation was carried out using graphite crystals. In the work described here, the AsF_5 intercalation methods which are given in detail (5,6) in the reports of the previous phases of this contract were applied to carbon/graphite fibers. Electrical resistivity and atmospheric stability were determined on the bare fiber. Composite resistivity and reflectivity were determined after compositing in an epoxy matrix.

SECTION II

EXPERIMENTAL PROCEDURES

1. Materials

Since most of the experiments were addressed directly to the problem of determining operating conditions for the intercalation of graphite fiber, most of the intercalation reactions were run directly on fiber. Celanese GY70 and Union Carbide Type P fiber were used throughout. Nitric acid was prepared in the laboratory by distilling HNO_3 from a mixture of H_2SO_4 and KNO_3. Commercial AsF_5 was used without additional purification.

Epoxy-fiber composites were prepared from commercial epoxy Stycast #1264. In our early experiments, uniaxial composites of 10-30 volume % fiber were layed up by hand and cured at room temperature under a nominal 5-pound load. Later, the specimens were cured under a 2000-pound load in a Carver Press at room temperature. This latter technique made it possible to prepare samples of nearly 50 volume % fiber. In various runs which were made to clarify some points concerning intercalation rates, and to scout alternative chemical routes to high conductivity, intercalation experiments were conducted with highly oriented pyrolytic graphite (HOPG) crystals, kindly supplied by Union Carbide through the good offices of Dr. Arthur Moore.

2. Intercalation Equipment

A special apparatus was built for gas-phase intercalation of graphite fiber. In essence, it is an elaboration on the set-up used in this laboratory for studies on the kinetics of intercalation of HOPG crystals.

It is shown in Figure 1; more details of the apparatus and its operation are given in reference (2).

Essentially, the intercalation unit consisted of a glass vacuum manifold connected to an intercalation chamber, nitric acid reservoir, AsF_5 supply, mercury manometer (protected by a 3 cm layer of oil), vacuum manifold and liquid nitrogen traps. The intercalation chamber was fitted with a quartz pan attached to a quartz spring balance. Weight increase of an HOPG crystal, or length of graphite fiber tow, could be monitored by following the extension of the spring with a cathetometer. In addition, the intercalation chamber was fitted with a glass rack upon which a larger quantity of graphite fiber tow could be loosely wound. It was established experimentally that the short piece of tow resting on the quartz pan experienced the same relative weight increase as the large tow at the bottom of the intercalation chamber. It follows, therefore, that there was no significant concentration gradient of intercalant gas in the reactor, and that the reaction rate was not controlled by diffusion of gas to the fiber surface.

3. Resistivity: Theory and Experimentation

Experimental study of electrical resistivity in epoxy matrix composite materials shows a strong dependence on the filling factor f. The resistivity varies as $1/f^n$ where n is between 7 and 12, inclusive. The value n appears to depend on the orientation of the fibers in the matrix and upon the type of material. We find that n = 12 for unidirectional (180^o) graphite fibers, $n \sim 9.5$ for fibers at 90^o and

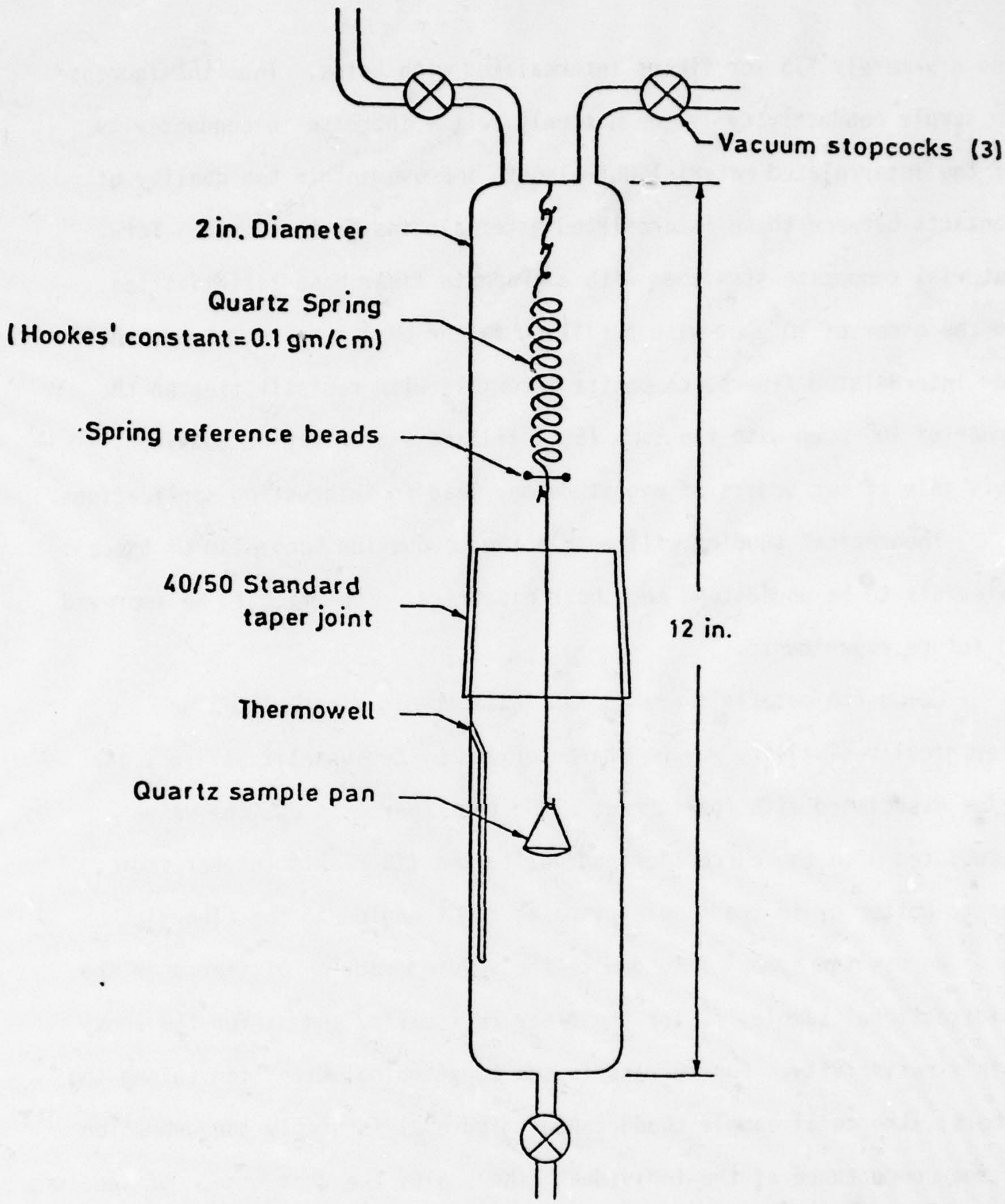


Figure 1. Apparatus for intercalation measurements

and n = merely 7.5 for fibers intercalated with acids. Thus the increase in sample conductivity is due not only to the increase in conductivity of the intercalated material but also to improvement in the quality of contacts between these intercalated materials inside the resin. For material composite standards with a graphite fiber base resistivities on the order of $10^6\,\mu\Omega$cm with a filling factor of 50% are obtained; while for intercalated fibers, composite materials with resistivities on the order of $10^4\,\mu\Omega$cm with the same (50%) filling factor may be obtained. This gain of two orders of magnitude may lead to interesting applications.

Theoretical studies will enable the conduction mechanism of these materials to be understood and their electrical properties to be improved in future experiments.

Composite materials are in fact anisotropic materials. The electrical resistivity may be characterized by two quantities: ρ_L, the value associated with the current along the fiber axis ρ_T, the value associated with the current orthogonal to the fiber axis (either from top to bottom or in the sample plane at right angles to the fibers).

We use the symbol f to denote the volume fraction of fibers in the unidirectional sample, ρ_1 for the fiber resistivity and ρ_2 for the epoxy matrix resistivity. For current in the longitudinal direction (along the fibers), the total sample conductance (figure 2) is simply the summation of the conductance of the individual fibers plus the conductance of the epoxy. It follows that the longitudinal resistivity may be written as:

$$\frac{1}{\rho_L} = \frac{f}{\rho_1} + \frac{(1 - f)}{\rho_2}$$

The calculation of the transverse resistivity is significantly more difficult.

4. Transverse Resistivity

The following two extremely simple models can be used to calculate transverse resistivity

a) the random fiber model

b) the distributed contacts model

Combining these two models makes it possible to formulate a theory that fully accounts for the electrical properties of the composite materials.

a. Random Fiber Model

The transverse resistivity is to be calculated for current through a series of parallel planes. The fibers are distributed across each plane with a probability f, the macroscopic volume of the fibers. For a sample composed of n such planes (figure 3), the transverse resistivity is calculated under the assumption that the boundaries of the two layers are equipotentials. Each vertical current tube may contain a number p of fibers such that $0 \leq p \leq n$, the probability of the tube containing p fibers being:

$$\text{Prob}(p) = C_n^p f^p (1-f)^{n-p} \tag{1}$$

The reduced resistance from such a tube is equal to:

$$R(p) = \rho_1 \cdot p + \rho_2 (n - p) \tag{2}$$

which yields the following average transverse resistivity:

$$\rho^{-1} = \sum_{p=0}^{n} \frac{C_n f (1 - f)^{n-p}}{\dfrac{\rho_1 \cdot P + \rho_2 (n - p)}{n}} \tag{3}$$

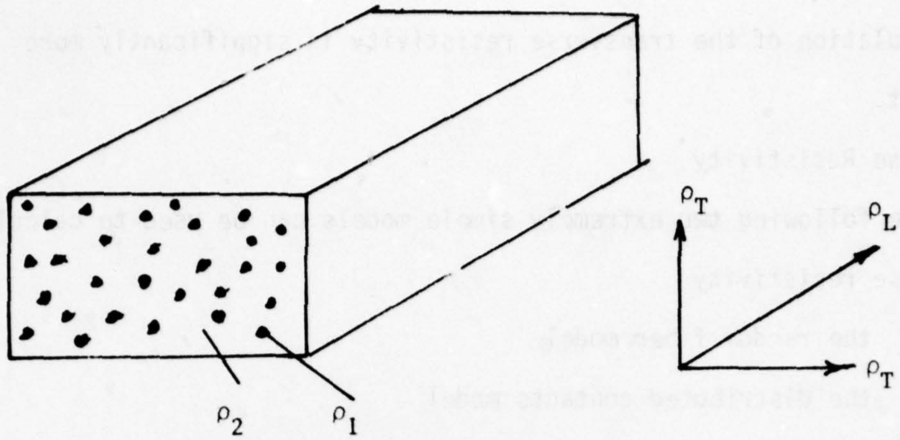


Figure 2 - Random Fiber Model

$\rho_{1,2}$ - resistivity of fiber and matrix respectively

$\rho_{T,L}$ - composite resistivity, transverse and longitudinal respectively

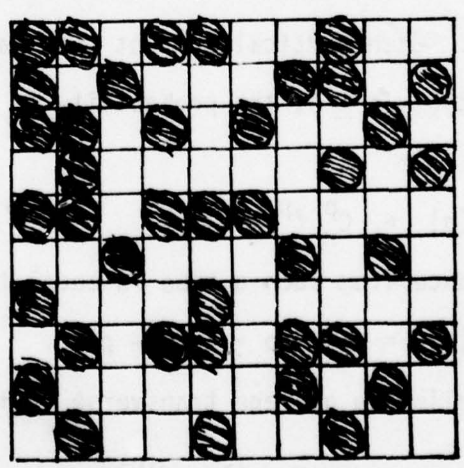


Figure 3 - Random Fiber Model. Resistivity of Fiber in cross section at

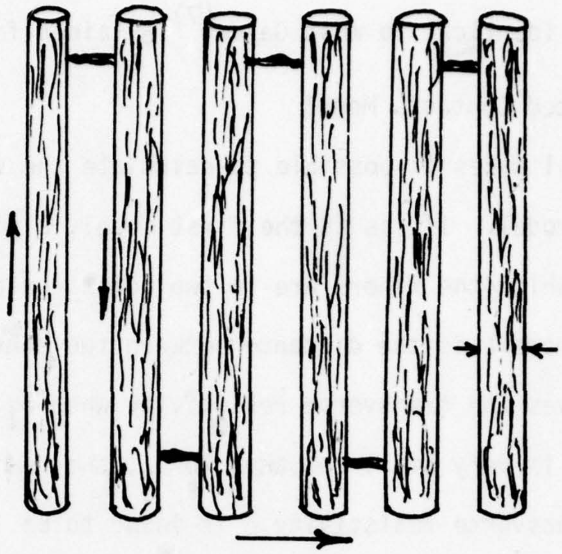


Figure 4 - Transverse Resistivity Scheme
See Equation (4)

This result is identical to what Gajda[7] obtained for $n = 2$.

b. Distributed Contacts Model

This model makes it possible to calculate the value of n used in the preceding model. If, as in the first model, a plane of fibers is considered in which the fibers are in two point contact as shown in Figure 3 and where L is the distance between two contacts, a simple calculation gives the transverse resistivity when ρ_1, the resistivity of the fibers, is very small compared to ρ_2, the resistivity of the epoxy. The transverse resistivity ρ is found to be

$$\rho = \frac{4}{\pi} \left(\frac{L}{d}\right)^2 \rho_1 \tag{4}$$

where d is the diameter of the fibers.

c. Calculation of n

The two models may be compared by letting the filling factor $f = \frac{\pi d^2}{4a^2}$ where d is the diameter of the fibers and a the average distance between fibers. Letting $\frac{L}{a} = n$ and considering only the principle term of equation 4 the following is obtained by combining (3) and (4):

$$n^2 = \frac{1}{f^{(n-1)}} \tag{5}$$

This relationship applies only to the maximum filling factor. Solving equation (5) for $f = f_o$ yields the following results:

$n = 10 \quad f_o = 0.599$
$n = 12 \quad f_o = 0.636$
$n = 14 \quad f_o = 0.666$

These results are consistent with experimental measurements even though the theory could be greatly improved.

5. Samples

Samples of the composite material are made from graphite fibers having a diameter of about 10 μ. The standard dimensions of the samples are about 35mm x 35mm x 3mm, with the fibers lying parallel to the sample surface. The filling factor varies from 0.35 to 0.55 depending on the sample and is determined by the mass of fibers included in the sample.

The resistivity of the starting fibers (pure or intercalated graphite) has also been measured by an induction method but these measurements have been made on closed loops in which the contact has been made with silver or gold paste.

These direct measurements have given resistivity values on the order of 500 - 600 μΩcm for graphite fibers and resistivity values approaching 120 μΩcm for graphite intercalated with nitric acid.

6. Other Experimental Procedures

Mechanical properties of composite specimens were determined on a bench-top Instron testor. Shear strengths were determined on lapsed specimens with the fiber $\pm 45^{\circ}$ to the axis of compression.

Stability of the electrical properties of intercalated fiber was determined by exposing the fiber to an atmosphere of 90-100% relative humidity at 180°F. The humidity chamber was a vacuum desiccator half filled with water and maintained at the proper temperature.

A tow of fiber was supported just above the water, and its electrical resistance was measured continuously; gold leads connected the tow to a Keithly VTVM.

Infra-red reflectivity of composite specimens were measured by Robert Winn of the Non-Metallic Materials Division of the Air Force Materials Laboratory.

A combustion train was set up for chemical analysis of the product intercalation compounds. The project was, however, terminated before the analytical method could be worked out in detail.

SECTION III

RESULTS

1. Process Conditions

These experiments were the first to demonstrate that a graphite fiber tow could be successfully intercalated to enhance its electrical conductivity with no serious (or obvious) degradations of physical properties, and that the intercalated fiber could be successfully incorporated into an epoxy composite.

In earlier experiments with HOPG[4] it was established that the best electrical conductivity of graphite could be obtained by first intercalating the crystal to stage 4 with nitric acid, then removing the labile HNO_3 molecule under vacuum, and reintercalating with AsF_5. We did not attempt to replicate the same increases in electrical conductivity with graphite fiber as was demonstrated for HOPG. This research focussed on the general process of preparing intercalated tow and incorporating it in an epoxy composite.

The first set of runs was made to compare the kinetics of the gas-phase intercalation of graphite fiber by nitric acid with that for HOPG crystals. Except for intercalation rates, the reaction between HNO_3 and graphite fiber demonstrated all of the earmarks of the same reaction carried out with HOPG (See Appendix and Ref. (2) for typical results with HOPG). After an induction period of 1-20 minutes, brown gas was evolved at the surface of the tow and the sample suspended from the quartz began to pick up weight. Graphite fiber does, however, intercalate far more slowly than HOPG. For a given set of conditions, intercalation rate of GY-70 fiber was about (1/20) of that for HOPG and that of the pitch base fiber was only (1/3) of that for HOPG.

To establish that the intercalation experiments were reproducible, four runs were made with each of the two fibers under the same conditions (fiber temperature = $30^{o}C$, acid temperature = $25^{o}C$). Induction period seemed erratic. From the time that intercalation began, however, the per cent weight was reproducible to about $\pm 15\%$ for any reaction time. Typical room temperature results are shown in Figures 5 and 6.

In Appendix A, we show that the rate of intercalation of HNO_3 into the graphite lattice is diffusion controlled. Clearly then, since the rates of intercalation of graphite fiber are even slower, rates must be controlled by diffusion through amorphous carbon to crystalline sites. The difference in rate of intercalation of GY-70 and pitch based fiber can be explained by difference in orientation of the crystallites. In the GY-70 fiber, the a-axes are parallel to the fiber axis and normal to fiber surface. This makes the crystalline regions of the pitch based fiber more accessible to the intercalating species, at least on the surface of the fiber, than in the GY-70.

Once the graphite fiber was intercalated to stage 2 with nitric acid, the neutral spacer molecules could be removed under vacuum to give a stage 4 compound (as determined by net weight gain). The vacuum in the intercalation chamber was then broken with AsF_5, and AsF_5 pressure brought up to half an atmosphere.

AsF_5 then intercalated rapidly and the reaction stopped at about a stage 3 compound (as determined by weight gain). We use the term stage very loosely here, because the mixed intercalation compound of HNO_3

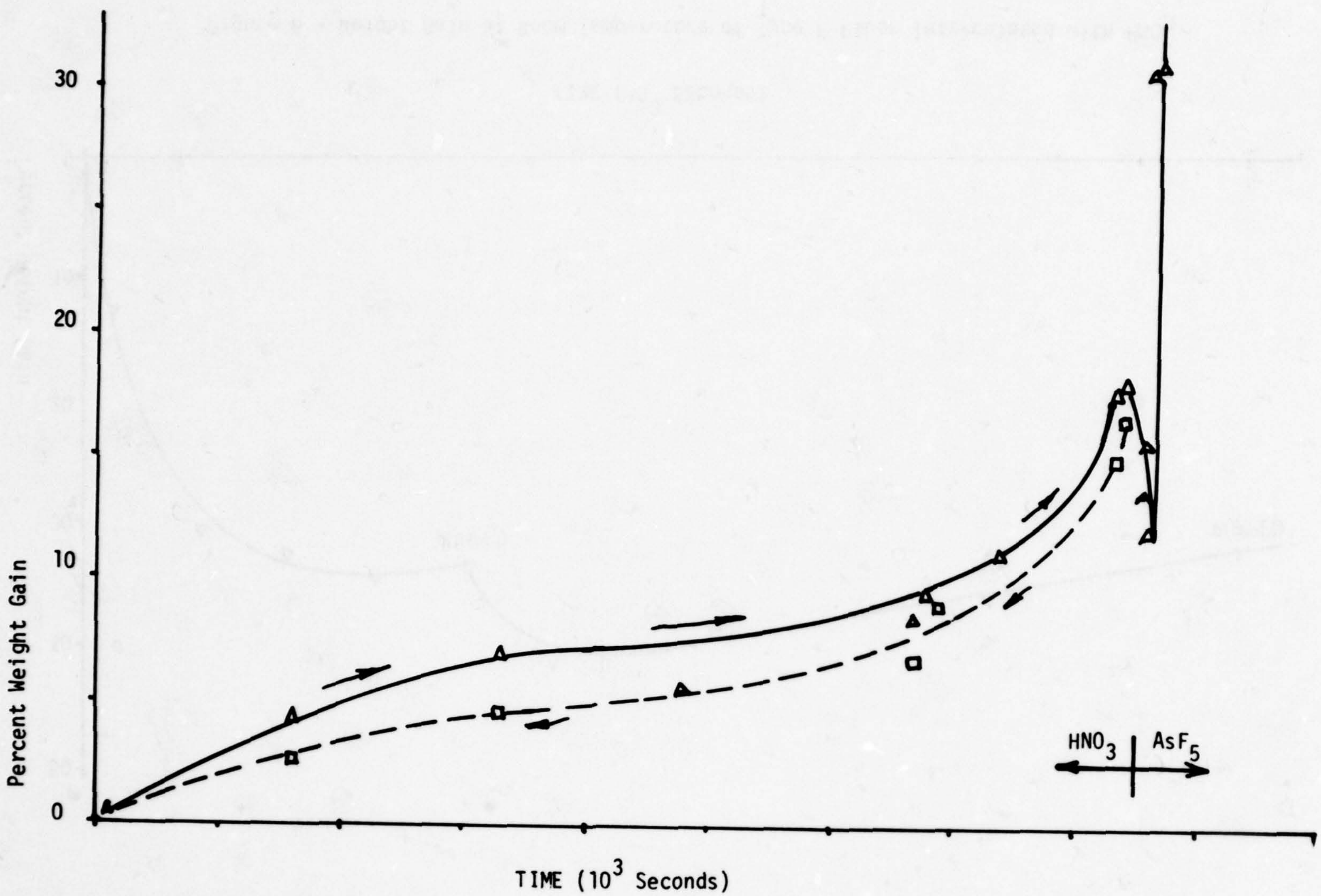


Figure 5 - Weight gain of GY70 Fiber Intercalated at Room Temperature with Nitric Acid and AsF_5
□ pump down

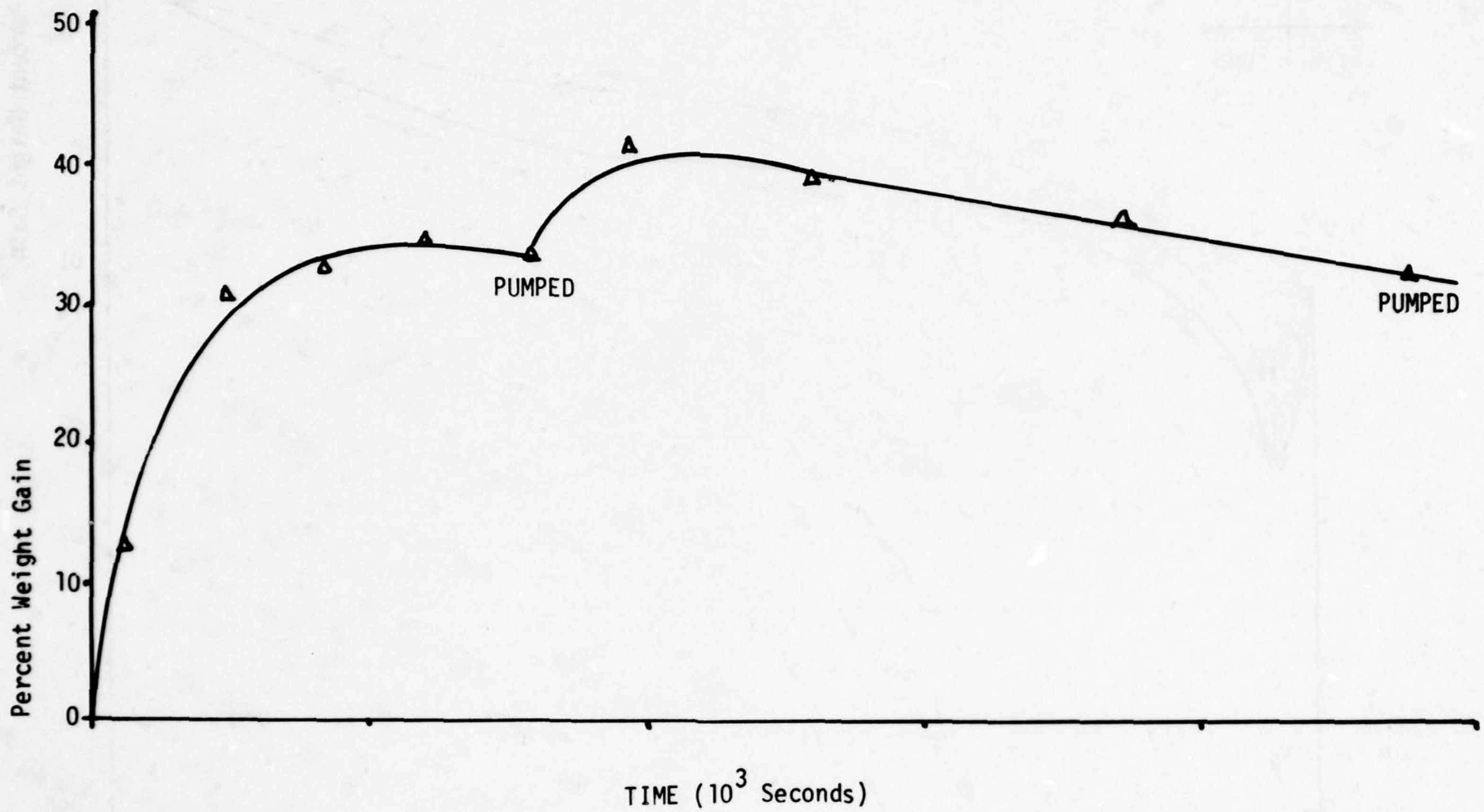


Figure 6 - Weight Gain at Room Temperature of Type P Fiber Intercalated with HNO_3

and AsF_5 has never been characterized - it is simply known that this compound demonstrates excellent electrical conductivity when formed from HOPG.

The AsF_5 reaction was complete in one hour. Clearly then, the HNO_3 intercalation is the critical step in the process kinetics, so all further kinetics experiment focussed on that step.

We examined the effect of temperature on the intercalation rate of HNO_3 on HOPG and both pitch base and GY-70 fibers. We found from the HOPG experiments that intercalation rates could be increased by a factor of five by running the reaction at a pressure near one atmosphere - fiber temperature = 80^oC and acid temperature 77^oC (the normal boiling point of HNO_3 is 80^oC). This, however, caused one unexpected difficulty. When a vacuum is pulled on the system to remove the labile HNO_3 from the lattice, the internal pressure of these HNO_3 neutral spacer molecules is so high that violent exfoliation of the lattice occurs.

Exfoliation could, however, be prevented by first cooling the acid reservoir and allowing the neutral spacers to "distill" slowly out of the lattice into the (slowly cooling) acid reservoir. Alternatively, we found that if we pulled a vacuum on a fully intercalated crystal <u>very</u> slowly, neutral spacers could be removed without destroying the crystal. Time did not permit further qualification of these procedures. Runs using fibers confirmed that intercalation rates could indeed be increased by a factor of five by running at elevated temperatures as long as neutral spacers were removed very slowly.

All further intercalation experiments, i.e. those run to prepare intercalated fiber for composite fabrication and testing were run at room temperature.

One aspect of our high temperature work was, however, both intriguing and somewhat disconcerting. We noted that the HOPG intercalation compound prepared at high temperature (acid at 77^oC, HOPG at 80^oC) had a significantly smaller proportion of labile HNO_3 to ionic content (NO_3^- ions) for any given weight gain than the compound prepared at room temperature. If this were true, the high temperature product should be a better conductor of electricity than the low temperature product. This turned out not to be the case. A high temperature product of stage 4 (by weight increase) demonstrated a volume resistivity of about 13×10^{-6} Ωcm whereas the usual stage 4 products demonstrated a value of 3×10^{-6} Ωcm. This should be looked at more carefully, since it is not clear at this point whether the high temperature fiber product would be better or worse than that intercalated at room temperature. Time did not permit further study of this phenomenon.

2. Aqua Regia Intercalation

This study is given a separate section of the report since it was a rather singular aspect of the research. We conducted an intercalation experiment replacing the nitric acid by aqua regia - an equal molar mixture of HNO_3 and HCl. The intercalation was carried out under conditions equivalent to our room temperature intercalations, went at essentially the same rate, and gave indication of going to a lower stage. There was, however, one important difference.

Commercial reagents were used and not specially prepared anhydrous HNO_3. The product had all of the outward appearances of the nitric acid compound and demonstrated a somewhat better electrical conductivity The process would, however, be much cheaper than the usual HNO_3 intercalation because of the use of cheaper starting materials.

We suggest the following mechanisms:

$$HNO_3 + 3HCL \rightarrow NOCl\uparrow + Cl_2\uparrow + 2H_2O$$

Nitrosyl chloride, NOCl, is a powerful oxidizing agent. The next step in the reaction is probably

$$NOCl + HNO_3 \rightarrow NO^+ + NO_3^- + HCl$$

(adsorbed on graphite) (adsorbed on graphite)

$$NO^+ + C \rightarrow C^+ + NO\uparrow$$

(adsorbed) graphite

$$NO + 2HNO_3 \rightarrow H_2O + 3NO_2$$

(vapor phase)

$$C^+ + (n - 1)C + NO_3^- + mHNO_3$$

$$\rightarrow C_n^+ NO_3^- \cdot mHNO_3$$

(insertion process) (intercalation compound)

Compare this mechanism to that for straight HNO_3 intercalation given in Appendix A. Since H_2O is not involved in the critical oxidation step for this new process, as is the case for intercalation by nitric acid, the reaction is not inhibited by H_2O.

If indeed the product formed by intercalation by aqua regia is graphite nitrate, we will have discovered a significant process improvement. This aspect of the program should be looked at most carefully.

3. Conductivity

With the induction method used, only the average of the transverse and longitudinal resistivities (ρ_T and ρ_L) respectively can be measured. In fact the transverse resistivity dominates so the resistivity measured is practically equal to the transverse resistivity of the composite material.

A logarithmic plot of the resistivity as a function of the filling factor is shown in Figure 7 and the resistivity values are given in Table 1. After having previously measured the resistivity ρ_1 of the starting material it is possible, knowing the resistivity ρ of the composite, to calculate the index n by the following formula:

$$n = \frac{\log (\rho_1/\rho)}{\log f}$$

This formula does not take into account the resistivity of the epoxy since it is much larger than the resistivity of the fibers ($\rho_2/\rho_1 \sim 10^{13}$). The values found for n are in agreement with the electrical resistivity theory for a unidrectional material. The theory has shown that n is related to the distance between the contacts on the fibers; the smaller the value of n, the smaller the resistivity. For unidirectional graphite fibers the value of n is about 12, for fibers oriented at 90^o n is significantly smaller, about 9.5. The exponent n is definitely smaller, about 7.5 for intercalated

fibers (HNO_3, AsF_5) whether the fibers are oriented in the matrix at 180^0 or at 90^0. A more complete theory is necessary for an in-depth understanding of the resistivity mechanism. In any case, the use of intercalation graphite fibers decreases significantly the resistivity of these materials; we have obtained a gain of about 100 compared to standard materials.

Calibration procedures and results are given in Figure 8 and Tables 2-4.

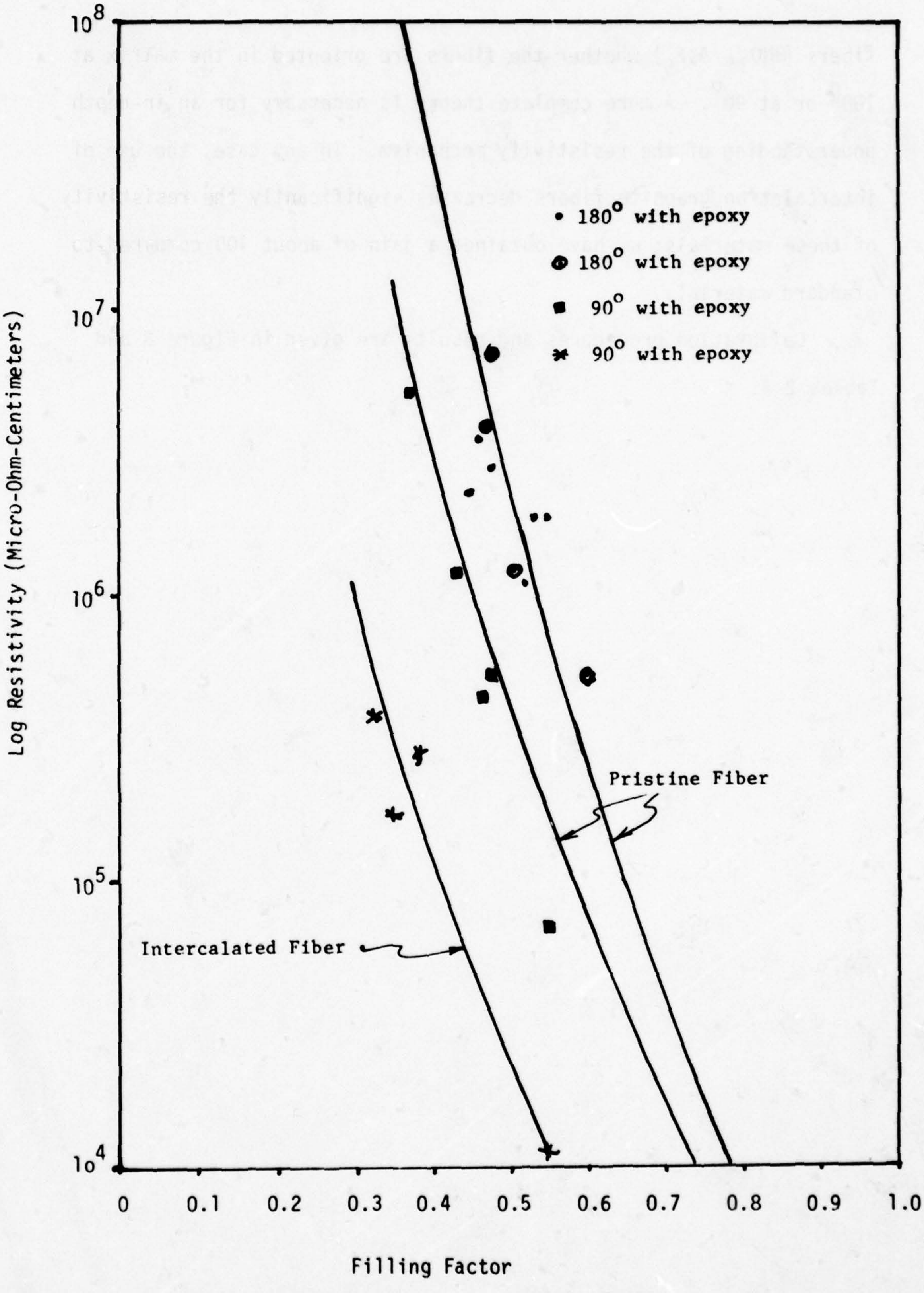
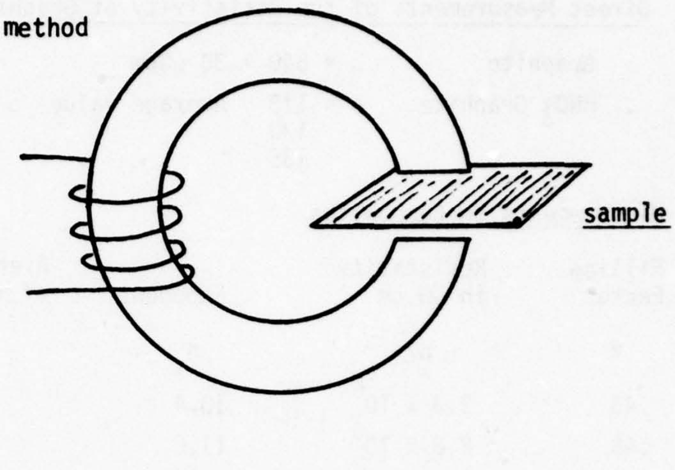


Figure 7 - Composite Resistivity vs. Filling Factor

Measurement of resistivity by induction method

1 kHz - 100 kHz

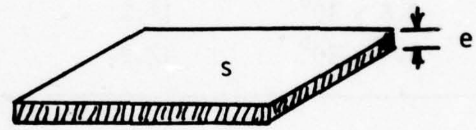
<u>Contactless Resistivity Method</u>



<u>Two types of samples</u>

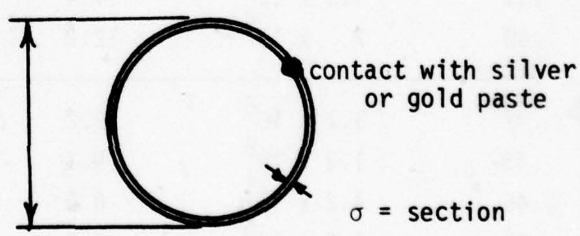
a) massive - square plates

Theory → $\Delta V = \dfrac{kes^2}{(1 + \alpha s^2)\rho}$



b) loops - practical for measuring the starting material (graphite fibers)

$$\Delta V = \frac{K'D^3\sigma}{(1 + \alpha' D^4)^2 \rho}$$



Note: The cross section of the fibers is determined by weighing given lengths of the fibrous materials and by using the theoretical density of graphite (δ = 2.27 g/cm^3)

The constants K, α, K', α' are calibrated using various materials - sheets - threads of various dimensions

Figure 8 - Method and Calibration of Composite Samples (above) and Fiber (below)

Table 1 - Summary of the Results of the Resistivity for Composites

Direct Measurements of the Resistivity of Graphite and HNO_3 - Graphite Fibers

Graphite $\rho = 540 + 30\ \mu\Omega cm$

HNO_3 Graphite $\rho = 113$, 130, 135 Average value $\bar{\rho} = 120\ \mu\Omega.cm$

Measurements On Composites

Filling Factor f	Resistivity in $\mu\Omega$.cm ρ	Exponent n	Average Value of the Exponent	Type of Ply	
.45	2.3×10^6	10.4			
.48	2.8×10^6	11.6			
.52	1.1×10^6	11.6	$\bar{n} = 11.9$	180^o	with epoxy
.55	1.9×10^6	13.6			
.46	3.6×10^6	11.3			
.53	1.9×10^6	12.9			
.25	-	-			
.35	$9. \times 10^7$	11.4			
.47	3.8×10^6	11.7			
.51	1.2×10^6	11.4	$\bar{n} = 11.8$	180^o	with epoxy
.48	$7. \times 10^6$	12.9			
.37	5.1×10^6	9.2			
.43	1.2×10^6	9.1			
.46	4.2×10^5	8.6	$\bar{n} = 9.54$	90^o	with epoxy
.47	5.5×10^5	9.2			
+ .55	6.7×10^4	11.6			
.33	3.8×10^5	7.3			
.35	1.7×10^5	6.9	$\bar{n} = 7.45$	intercalated fibers + epoxy	
.38	2.8×10^5	8.0			
+ .55	1.1×10^4	7.6			

+Sample prepared under pressure

Results for Composite Materials

- • ⊗ pure graphite composite at 180^o
- ■ pure graphite composite at 90^o
- ✱ intercalated graphite composite

Table 2 - Calibration with Thin Square Plate

Metal	Thickness e_{mm}	Surface area s_{mm^2}	Signal ΔV mv	Resistivity $\rho_{\mu\Omega \cdot cm}$	Calibration Resistivity K^{-1}
Al	.015	900	290	2.8	14.9
Brass	.13	700	546	7.4	12.3
Tantalum	.15	1400	750	15.5	24.5
Pb	.46	1450	1710	22	25.7
Manganin	.35	730	314	44	12.6
Gold alloy	.12	400	134	14	9.52
Zinc	0.2	2025	3230	6.1	42.3
German silver	.68	320	233	33	9.05

$$K = \frac{0.122}{1 + \alpha s^2} \qquad \alpha = \frac{1}{(31.4)^4}$$

Table 3 - Measurement of the Resistivity of Graphite Fibers by the Loop Method

	Resistivity of Graphite Fibers				Cross-section Measurement density of graphite $d = 2.27$		
	Diameter of the Loop D	Cross Section σ	Signal ΔV	$\rho\mu r.cm$	Length E mm	Mass m	Cross-section σ mm^2
A	35.5	.54	5.02	540	238	291.7	.54
B	33.2	.28	2.64	596	243	154.5	.28
C	38.4	.32	2.18	620	221	160.5	.32
D	41.2	.46	2.90	552	252	263.1	.46
E	36.3	.39	3.07	610	229	202.7	.39
F	32.9	.27	2.64	582	237	145.3	.27
G	37.8	.48	3.56	590	248	270.2	.48

$m = E\,\sigma\,\delta$ m = Mass
E = Length
σ = cross-section
δ = density

Table 4 - Calibration with Loop of Different Metals.

	Diameter on mm D	Cross Section σ_{mm^2}	Signal ΔV mV	Resistivity ρ $\mu\Omega$ cm
Cu	35.6	1.39	3300	2.1
Cu	25.7	0.82	2230	2.3
Brass	40.5	7.2	2960	3.9
Gold Alloy	20.8	0.07	23	15

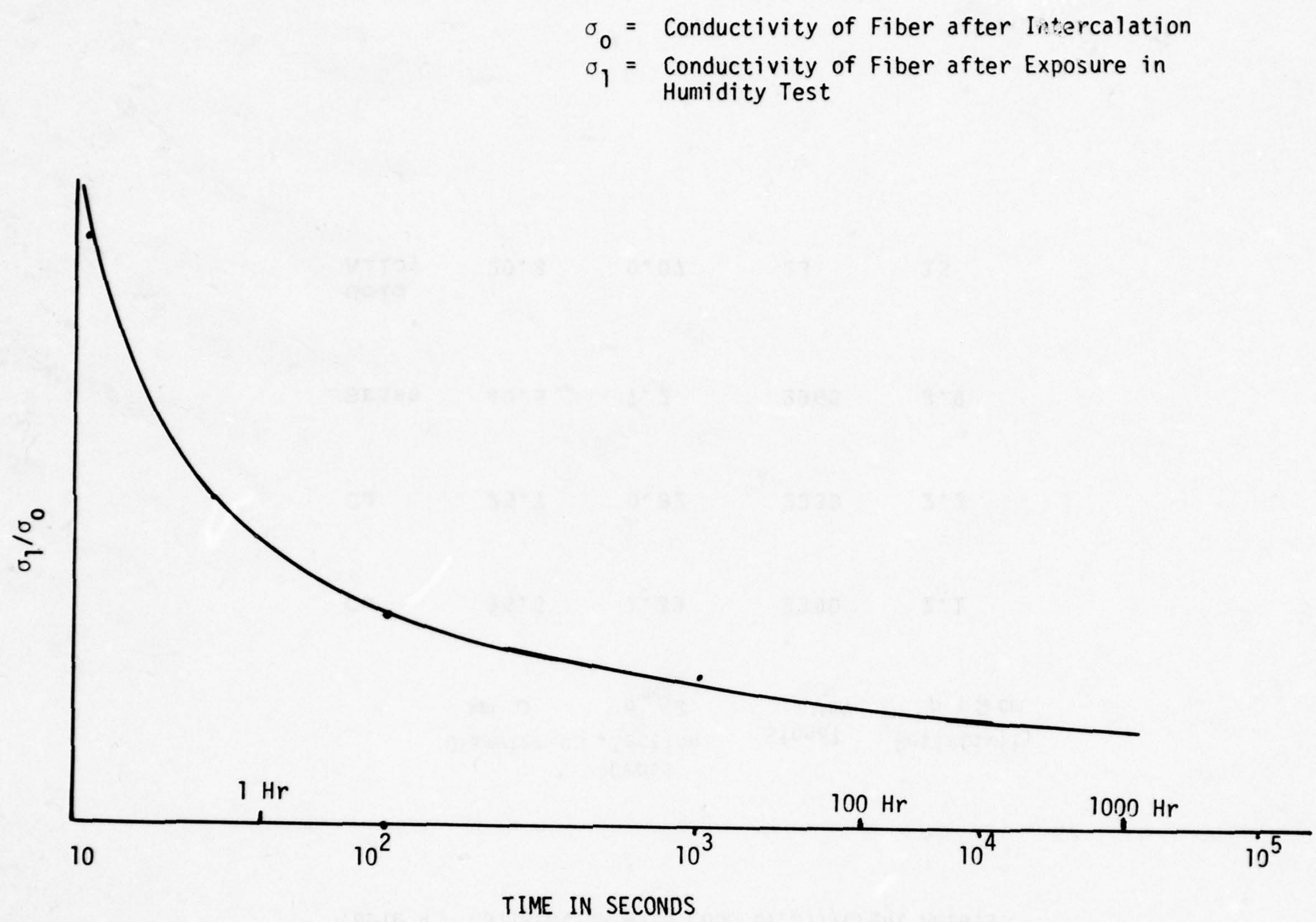


Figure 9 - Decay of Electrical Conductivity of Intercalated Fiber in Humidity Test.

Reflectivity Results

Graphite fiber reinforced epoxy samples for reflectivity measurements were prepared as previously described in this report. Reflectivity measurements were made in a double beam Willey Spectrometer at Wright Field with a total reflection sphere using an evaporated gold standard. The reflection spectra were taken in the range from 1 μ to 20 μ; results are given in Table 5 for 10.6 μ - the wavelength of greatest interest. The disappointing result of the first four samples was traced to a low volume percentage of fiber in the composite and so a set of samples with higher fiber density was fabricated and tested (Nos. 5 and 6). While the effect of higher density on reflectivity is immediately evident, the effect of intercalation with HNO_3 and AsF_5 on reflectivity is not.

Thus, we have to explain why the composites with intercalated fibers showed a high electrical conductivity whereas they did not exhibit high reflectivity in the infrared despite the fact that it had been shown previously that intercalation increases the IR reflectivity of graphite to substantially 100%. An explanation lies in the possible loss of intercalant from the surface layers before compositing. Fiber orientation is another possible explanation.

Table 5. Reflectivities of Fiber Epoxy Composites at 10. 6 μ Wavelength.

	Fiber Type	Volume Fraction Fiber	Total Reflection	Diffuse Reflection	Specular Reflection
		%	%	%	%
1 -	UCC TYPE P PRISTINE	–	3.6	3.0	0.6
-	UCC-P INTERCALATED	–	5.0	4.0	1.0
-	CELANESE GY-70 PRISTINE	29	20	6	14
-	CELANESE GY-70 INTERCALATED	8.6	10	8	2
-	CELANESE GY-70 PRISTINE	55	32	27	5
-	CELANESE GY-70 INTERCALATED	55	25	21	4

Fiber Stability

Figure 9 shows the ratio of resistance of intercalated fiber tow to its initial value as a function of time when the fiber is exposed to ~100% humidity at $180^{o}F$. Since intercalation increased conductivity of the fiber by a factor of 6-10, exposure to water vapor at $180^{o}C$ effects deintercalation in about 1000 hours. Conductivity is cut in half in about one hour. Clearly, the HNO_3-AsF_5 intercalation compound must be protected from such severe conditions - say by compositing with a hydrophobic polymer.

New Routes to Intercalation Compounds

A modest fraction of the support under this project was devoted to scouting for new and better intercalation compounds. A new class of intercalation reactions was discovered in this effort using nitronium and nitrosonium compounds. This gives us the capability of preparing a "stable" of new compounds from nitronium and nitrosonium salts. So far, however, we have prepared only rather poorly characterized compounds from gas-phase and solution reactions with NO_2BF_4,NO_2SbF_6, $NOSbF_6$ and $NOPF_6$ and we haven't been able to get the reaction of graphite with $NOPF_6$ to go in solution, perhaps because of impurities, and maybe because it isn't sufficiently ionized.

The gas-phase reactions with the vapor in equilibrium with nitronium salts were, in reality, reactions in equal molar mixtures of nitryl fluoride and a Lewis acid. For example, in the nitronium tetrafluorobroate reaction, the gas-phase was generated by the reaction.

$$NO_2BF_4 \rightleftharpoons NO_2F + BF_3$$

In all cases, rather high temperatures were required to effect dissociation (175-300^oC). A logical extension of this work, then, would be to perform the gas-phase intercalation in gas mixtures prepared from the constituent gases. This offers the advantage of being able to adjust the ratio of the two gases; some composition other than equal molar might be more effective as an intercalation medium. We should add, however, that little is known about the rate of reaction between NO_2F and most Lewis acid gases to give nitronium salts. Success depends upon maintaining a gas mixture that would not dissipate reagents by salt formation which is more rapid than intercalation.

It is clear, however, that if the gas-phase reactions are successful, they would be much "cleaner" and more convenient route to the same compounds. We would also have a completely independent method of checking the intercalation mechanism. *One mole of NO_2 should be formed for every* mole of electrons removed from the graphite.

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APPENDIX

Mobility of Spacer Molecules in Graphite Nitrate

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ABSTRACT

Neutral nitric acid molecules in graphite nitrate prepared from HOPG at 24°C with anhydrous nitric acid are labile and can be moved in and out of the lattice by adjusting the partial pressure of HNO_3. Both the initial intercalation and subsequent diffusion of HNO_3 into the lattice followed a simplified first-order rate model to a reasonable approximation. The rate constant was, however, somewhat higher for simple diffusion of HNO_3 into the lattice, than for the case when the graphite was being oxidized by the nitric acid.

A compound, intercalated to second stage by x-ray analysis and weight gain, demonstrated an electrical resistivity of $3.0 \times 10^{-6}\,\Omega$cm. When sufficient HNO_3 was removed under vacuum to give a net weight gain associated with a stage-4 compound, the product demonstrated the correct x-ray pattern for such a compound and the electrical resistivity remained essentially unchanged.

INTRODUCTION

Intercalation compounds of graphite have been receiving increasing attention over the last several years, with much of the interest stimulated by their interesting electrical properties (1). Nonetheless, many aspects of their structure and the mechanism (or mechanisms) by which they are formed remain ill-defined. This is particularly true with so called "acceptor" compounds formed by intercalation by metal halides in the presence of halogens, strong Lewis acids and protonic acids. In most cases, there are compelling arguments that the mechanism for formation of "acceptor compounds" is an attack on the graphite lattice by a highly electrophylic reagent (ion, molecule or complex), with concomitant diffusion of anions into the interlaminar regions (2). As ions diffuse into the lattice they are invariably accompanied by neutral molecules. At equilibrium, therefore, one would expect to find some well defined ratio of neutral molecules to ions.

Intercalation by nitric acid has been of considerable interest since the early work described by Rudorff and Hofmann (3), and summarized in 1959 by Rudorff (4). In a recent paper from this laboratory (5), we gave experimental evidence that this reaction proceeds as follows:

$$2HNO_3 \rightarrow H_2O + N_2O_5 \qquad (1)$$

$$N_2O_5 \rightarrow NO_3^- + NO_2^+ \qquad (2)$$

$$nC + NO_2^+ \rightarrow nC^+ + NO_2 \qquad (3)$$

$$nC^+ + NO_3^- + mHNO_3 \rightarrow C_n^+ \cdot NO_3^- \cdot mHNO_3 \qquad (4)$$

(intercalation step)

Reactions 1-3 would occur at the graphite-gas interface, with the product NO_2 desorbing as a gas. Evolution of NO_2 was measured by chemiluminescence techniques. The loss of a small amount of NO_2 inherent with this experimental method made it impossible to determine the value of m exactly, but since the source of error was well known, we were able to report that $m \lesssim 4.5$. More recently, Fischer, et.al. (6) determined the NO_2 formed by nitric acid intercalation, and reported that $m = 4.13 \pm 0.08$.

This implies that the stoichiometry for the stage-two compound should be $C^+_{60} \cdot NO_3^- \cdot 4HNO_3$ instead of $C^+_{48} \cdot NO_3^- \cdot 3HNO_3$ as reported by Ubbelohde (7).

The above considerations apply, of course, to intercalation compounds for which the HNO_3 molecules are in equilibrium with the NO_3^- ions. The presence of neutral molecules in the graphite nitrate compound suggests, however, that they might be removed and reintercalated by varying the partial pressure of HNO_3 without changing the oxidation state of the graphite. This research addresses itself to that subject.

EXPERIMENTAL CONSIDERATIONS

The experimental system used for this work has been described elsewhere (5). Intercalation reactions were run with samples of highly oriented pyrolytic graphite (HOPG) supplied by Union Carbide. Before an experiment, they were baked in a vacuum oven at 165°C for approximately 10 hours. Nitric acid was prepared on the vacuum manifold just prior to an experiment by adding H_2SO_4 from a dropping funnel to solid KNO_3 and condensing the product HNO_3 in a cold finger, which was then used as the acid reservoir.

During the course of the intercalation, the acid was kept at $20.0 \pm 0.1°C$ with a constant temperature bath. The HOPG crystal was kept at room temperature, which, for the experiment described here, was $24° \pm 1°C$. The progress of the intercalation was followed gravimetrically (5).

The following intercalation-deintercalation-reintercalation scheme was developed: The crystal was first exposed to pure nitric acid vapor, and the crystal weight gain was monitored. Intercalation proceeded, as described previously (5), with NO_2 evolution. The reaction went to completion at a weight gain between values reported for stage-one and stage-two compounds.[7] To effect deintercalation of the neutral nitric acid molecules, the vapor composition over the crystal was then changed from HNO_3 (and by-products H_2O and NO_2) to very nearly pure dry nitrogen. This was accomplished in steps. First enough nitrogen was added to increase the total pressure over the crystal from 42 to 62mm-Hg. This was done rapidly enough to effect some mixing of gases in the intercalation chamber. The system was then allowed to sit for several minutes until it became homogeneous to the eye (as determined by observing the brown color of NO_2). The system was then pumped back down to 42mm-Hg. This sequence was continued until the calculated nitric acid concentration in the vapor was reduced to less than 0.2mm-Hg. After several nitrogen additions, dilution of NO_2 made it impossible to judge the efficiency of mixing by eye, but since the same procedure was used each time, mixing should have been about the same for each step. During the gas exchange and for several hours after, the intercalated sample lost weight. When spontaneous deintercalation appeared to stop, the total pressure of the intercalation chamber was reduced in approximately 10mm increments until a vacuum of 1×10^{-4} torr was eventually pulled on the crystal.

Under vacuum, the intercalation compound lost a few more percent of its weight. During the deintercalation experiment, the crystal lost very nearly 1/2 of the weight gained from the intercalation reaction.

The stepwise procedure described above was necessary to prevent exfoliation. In an initial attempt to remove HNO_3 from a freshly prepared intercalation compound by pulling a hard vacuum on the system, exfoliation was so violent that the sample "jumped" off of the balance pan.

After deintercalation, the vacuum was broken with HNO_3 vapor, and the crystal began to intercalate immediately with release of NO_2 - but, obviously, with much less NO_2 than had been released during the initial intercalation. After intercalation ceased, deintercalation was effected a second time according to the routine described above. Again, after pulling off all of the HNO_2 that could be removed by a hard vacuum, the crystal was exposed to 42mm-Hg of HNO_3 vapor and reintercalation began immediately. This time, however, it was accompanied with only slightly preceptible NO_2 evolution. It was then deintercalated, and reintercalated for a fourth and final time. No NO_2 was observed in the final intercalation step.

The initial weight of the HOPG specimen and its weight after intercalation and deintercalation steps are shown below:

$$67\text{mg} \xrightarrow[\text{intercalation}]{} 117\text{mg} \xrightarrow[\text{deintercalation}]{} 89\text{mg} \xrightarrow[\text{reintercalation}]{} 112\text{mg} \xrightarrow[\text{deintercalation}]{}$$

$$96\text{mg} \xrightarrow[\text{reintercalation}]{} 104\text{mg} \xrightarrow[\text{deintercalation}]{} 96\text{mg} \xrightarrow[\text{reintercalation}]{} 104\text{mg}$$

Weight of the HOPG, for the initial intercalation and reintercalation steps as function of time are shown in Figure 1. Because of the stepwise nature of deintercalations, the results are not shown graphically.

DISCUSSION

We suggest the following interpretation of the above experimental results: The initial intercalation proceeded normally with evolution of NO_2, as reported previously (5, 6). In our previous work, however, intercalation in this temperature regime terminated at a weight gain close to that reported for a stage-two compound. In these experiments, however, the weight gain exceeded that for a stage-two compound. In our previous work (5), as in the work of others (8), the nitric acid was prepared by distillation. In these experiments, however, the HNO_3 was prepared on the vacuum line from KNO_3 and 98% H_2SO_4. Considering the dehydrating power of H_2SO_4, it is not unreasonable to assume that some N_2O_5 would distill over with the HNO_3. The amount must be small, however, since the vapor pressure of the acid was within $\pm$1mm-Hg of the reported vapor pressure of HNO_3 at the temperature of the nitric acid reservoir. Nonetheless, even a small quantity of N_2O_5 in the HNO_3 vapor could explain how intercalation proceeded beyond a weight gain associated with stage-two (7).

Since oxidation of graphite is irreversible, the first deintercalation could only be removal of the so called neutral "spacer" molecules - or HNO_3. Since one-half of the mass of intercalant was removed by diffusive deintercalation into 42mm-Hg of N_2 and under vacuum, one is tempted to write the stoichiometry.

$$C_n^{+}\ NO_3^{-}\cdot mHNO_3$$

when m is unity.

Ubbelohde (7), however, reports m=3 and Fischer et.al. (6) report a value of m=4. Work from this laboratory (5) gives m≲4. Either there is an inherent error in the determination of m, or only about 2/3 of the neutral HNO_3 molecules can be pumped off, the rest probably being stabilized by a resonance sharing of the proton.

That quantity of intercalant, not removed from the lattice after the weight had remained constant ($\pm$0.2mg) for 12-15 hours when the sample was kept under a hard vacuum, is referred to here arbitrarily as ionic intercalant, or NO_3^-. We will understand, however, that if the previous stoichiometries are correct (5-7), the ionic content must tie up molecular HNO_3 by sharing the protons. Given that qualified definition, then, we will say that the initial intercalation inserted 50mg of intercalant - 22mg of NO_3^- ions and "bound" HNO_3 along with 28mg of HNO_3 molecules, which were removed in the first deintercalation.

The first reintercalation clearly was accompained by further oxidation of the graphite lattice as evidenced by NO_2 evolution. More NO_3^- ions were thus being inserted into the lattice, along with HNO_3 molecules. Curiously, however, less total intercalant was inserted in the lattice during the first reintercalation than during the initial intercalation. This suggests that when fewer neutral spacers are intercalated, and "extra" ions are inserted, less total intercalant (for the same driving force) can be accommodated in the lattice, probably because of greater ion-ion repulsion.

Less HNO_3 was removed during the second deintercalation than during the first. This is, of course, consistent with the observation that the product of the first reintercalation, although containing less intercalant, is more ionic.

Quantitatively, we would say that the first reintercalation inserted 5 more mg of NO_3^- and bound HNO_3, and 16mg of labile HNO_3.

The second reintercalation and third deintercalation showed the same qualitative effect as the corresponding two processes preceding them, but there was very little additional oxidation of the lattice. Reintercalation again proceeded to a lower level of total intercalant which, upon deintercalation, was shown to be slightly more ionic; i.e., less neutral HNO_3 molecules were removed under vacuum. The final reintercalation and deintercalation steps, however, entailed nothing more than moving neutral HNO_3 molecules in and out of the lattice by adjusting the partial pressure of the nitric acid.

To examine the rate of intercalation in more detail, we postulate the following kinetic expression as representing the process:

$$\frac{dw}{dt} = k(W_m - W)$$

where W = weight of intercalant

W_m = maximum weight of intercalant

k = rate constant

This gives $\ln(1-\Theta) = -kt$

$$\Theta = W/W_m$$

This can be thought of as a first-order space-filling process, where the rate is proportional to the number of sights, or vacant positions, available to the intercalating species (molecules and/or ions).

Figure 2 gives a semi-log plot of (1-Θ) as a function of t. Only data to 45 minutes are included since experimental error is grossly exaggerated in the term ln(1-Θ) as Θ approaches 1.0. The rate data follow the simple, first-order model remarkedly well. The rate constants for the initial intercalation and the first reintercalation, for which the lattice is being oxidized, are nearly the same. Both are substantially smaller than for the second and third reintercalation, for which oxidation plays a small or negligible role, and diffusion of HNO_3 into the expanded lattice dominates.

In a replicate experiment, an HOPG crystal was intercalated carefully to second stage by weight, removed from the apparatus and x-rayed in an atmosphere of pure HNO_3. It indeed demonstrated the lattice spacing of a second large compound. Its specific resistivity was also measured by the contactless technique (9) and it gave a value of 3.0×10^{-6} Ωcm which is characteristic of a stage-two compound. The crystal was then returned to the intercalation apparatus, and the neutral spacer molecules removed as described above. As before, 1/2 of the initial weight gain was lost. The crystal was again removed from the apparatus and kept in an argon atmosphere while x-ray and electrical resistivity measurements were made. This time, the crystal demonstrated the lattice spacing of a stage-four compound, but the resistivity remained virtually unchanged at 2.9×10^{-6} Ωcm.

These results suggest that the electrical conductivity is related to the ionic content of the intercalation compound and not substantially affected by the presence of neutral spacers. This implies, at least in this case, that conductivity is related primarily to the extent of oxidation of the lattice.

In addition, these results cast doubt on the concept that the stoichiometry of an intercalation compound is independent of stage, or possibly that stoichiometry is even unique for a given stage. That is, we prepared what, by weight gain and x-ray analysis, was defined as a stage-four compound by removing neutral spacers from a stage-two compound. But does that stage-four compound have the same stoichiometry as one prepared by direct intercalation? Our experiment could not answer that question. We do, however, suggest that the concept of stoichiometry of intercalation being independent of stage deserves careful reconsideration.

ACKNOWLEDGMENT

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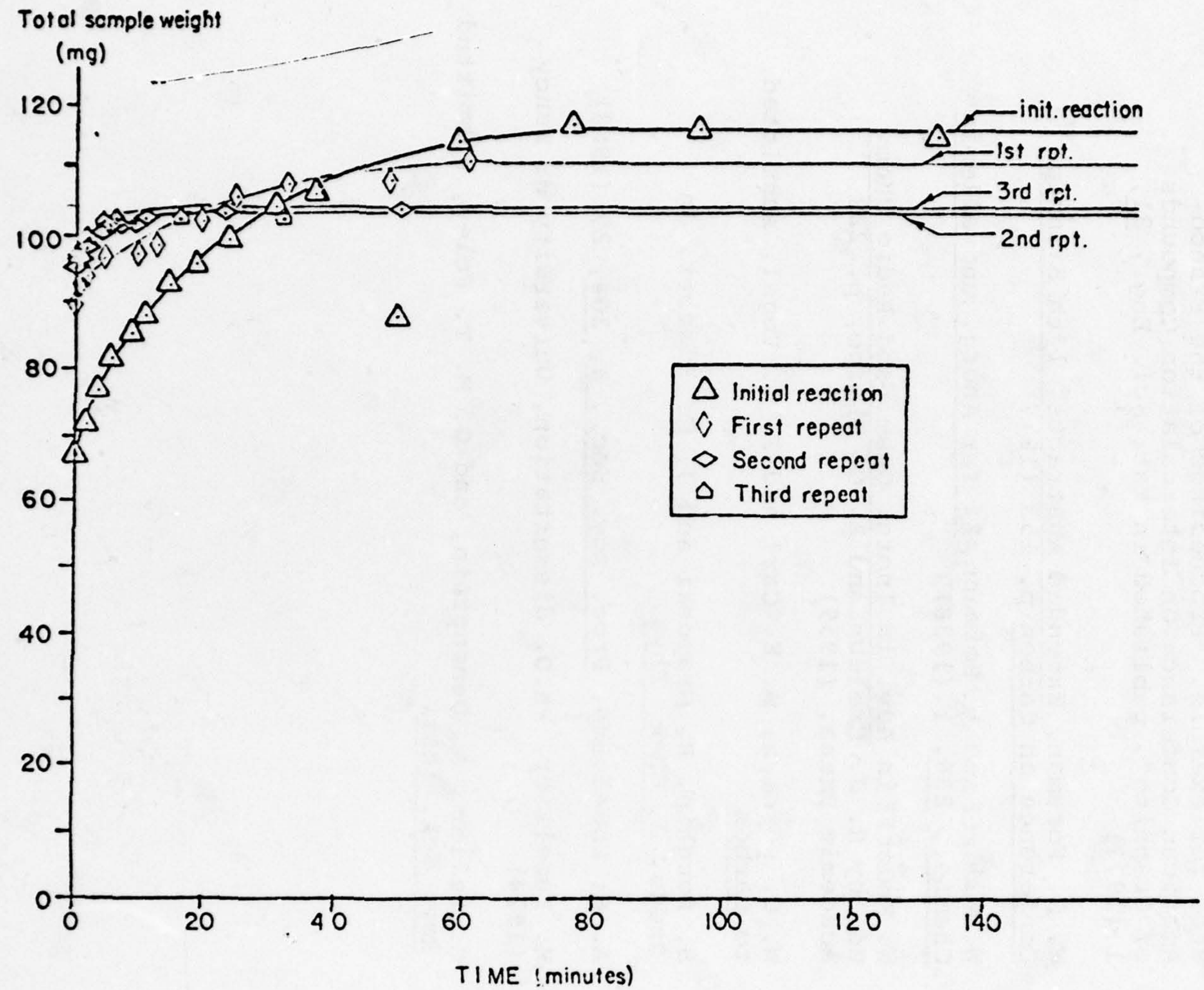

FIGURE 1 - Sample weight vs. time for initial intercalation and successive reintercalation.

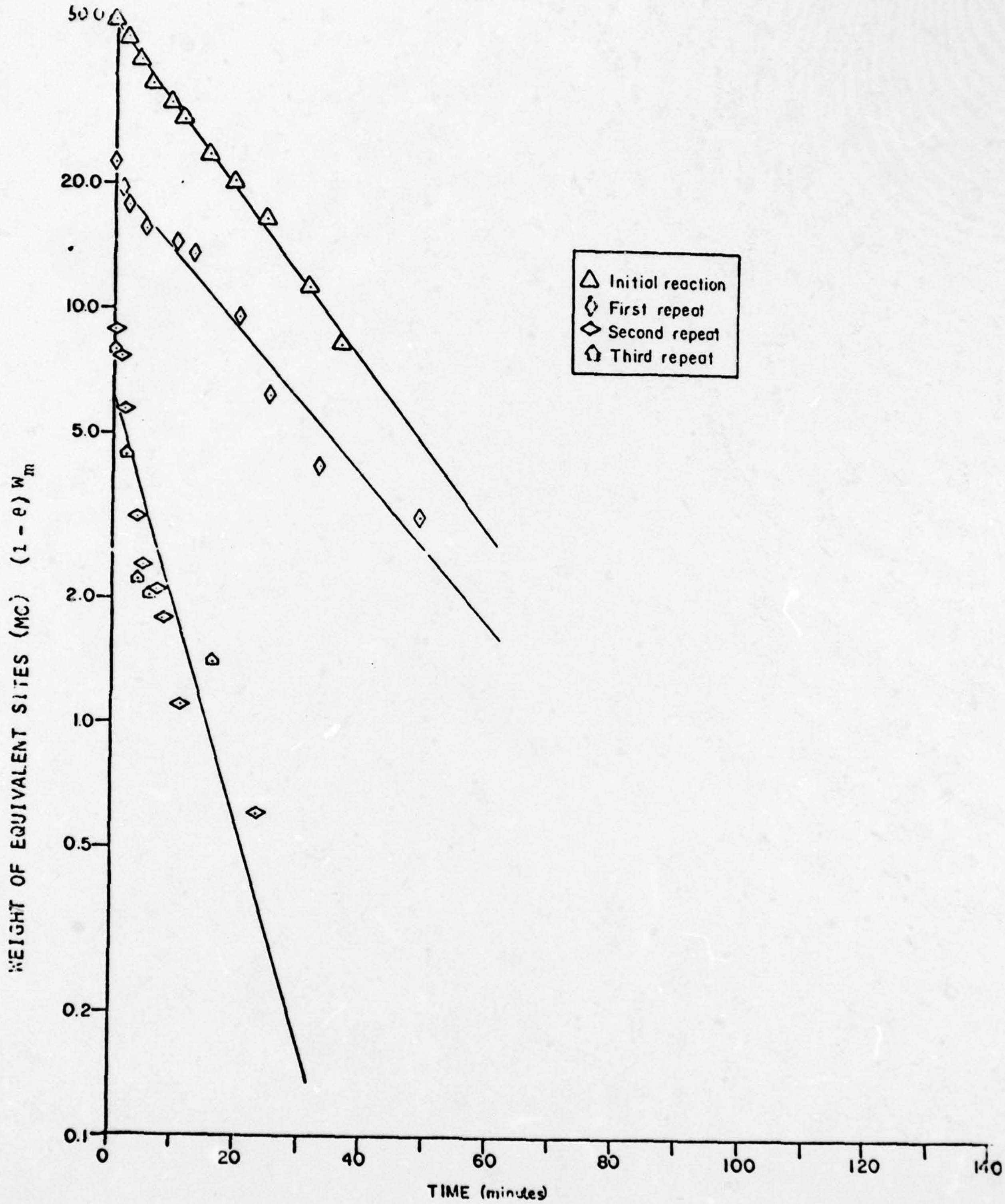

FIGURE 2 - First-order space filling model for intercalation reactions shown in Figure 1.

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